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Double Fluorides of
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DOUBLE FLUORIDES OF TANTALUM
AND COLUMBIUM

BY

LLOYD H. ALMY

THESIS FOR THE DEGREE OF BACHELOR OF SCIENCE

IN CHEMICAL ENGINEERING

IN THE

COLLEGE OF SCIENCE

OF THE

UNIVERSITY OF ILLINOIS

Presented June, 1909

1909
A26

1709
176

UNIVERSITY OF ILLINOIS

May 31 1909

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

LLOYD H. ALMY

ENTITLED DOUBLE FLUORIDES OF TANTALUM AND COLUMBIUM

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE

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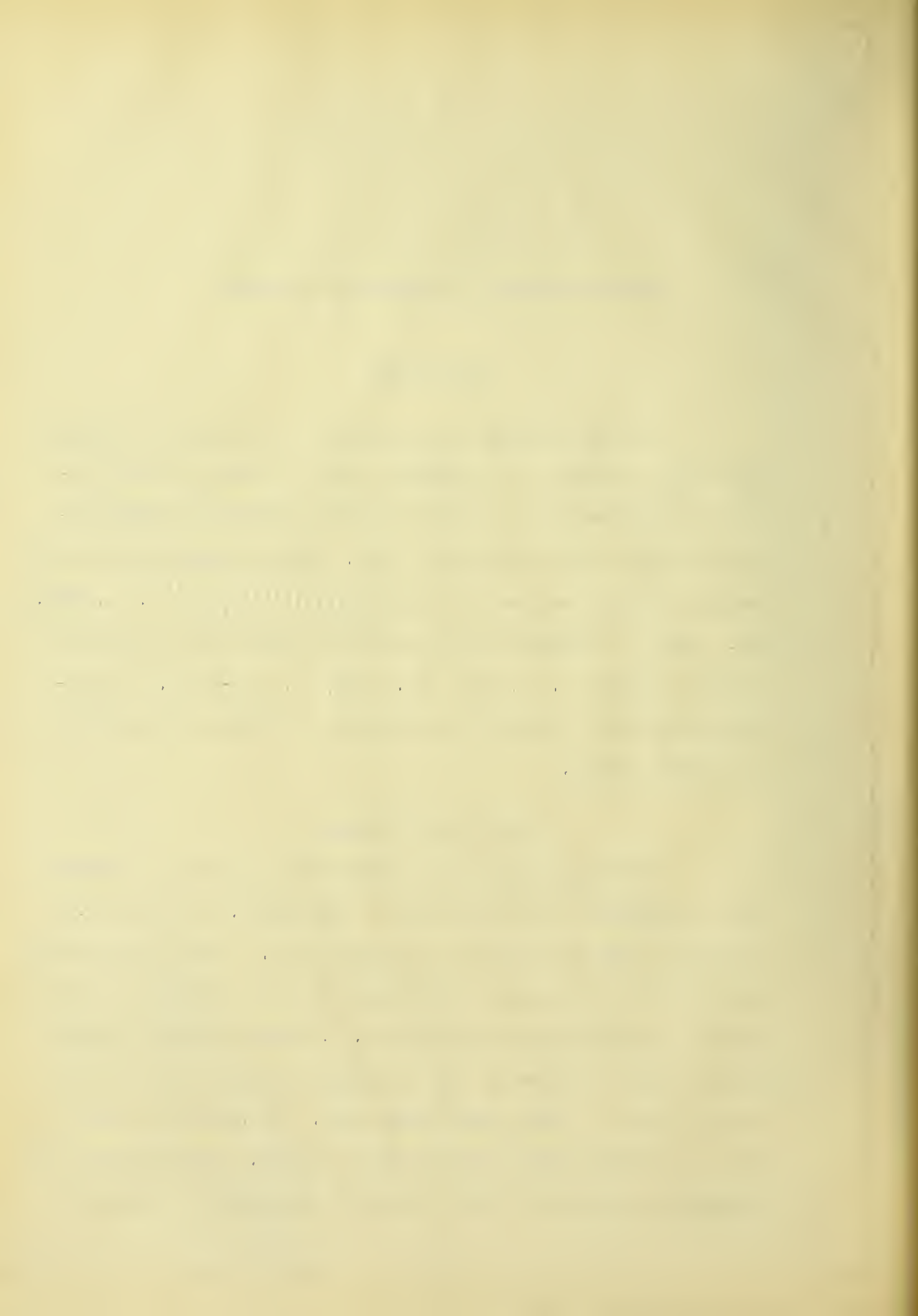
DOUBLE FLUORIDES OF TANTALUM AND COLUMBIUM

Introduction

On looking through the literature it was found that although many double fluorides of the metallic acids with metals had been prepared, comparatively few such salts had been prepared by bringing together metallic acids with organic bases. Among the latter are the compounds of titanium and the alkaloids prepared by Shaeffer (J. Am. Chem. Soc., 1908, 30, 1862-1865) and the pyridine tantalum double fluoride prepared by Balke (J. Am. Chem. Soc., 1905, 27, 1140-1157). This investigation deals with seven new compounds of tantalum and columbium of the above nature.

Preparation of Material

The material used in the present investigation was obtained from the columbite of the Black Hills, South Dakota. The mineral was ground fine enough to pass thru a 120 mesh sieve. It was then fused in iron crucibles with potassium hydroxide, one part of mineral to three parts of potash giving the best results. The mass fused very quietly from the first, provided the heat was applied gradually using finally the full heat of a three burner Bunsen lamp. The action was complete when the solution became pasty and green in color. The fused mass upon cooling was covered with water to dissolve the potassium tantalate and



columbate formed. The solution was filtered and a small portion tested for manganese, which was not found. The filtrate was treated with sulphuric acid, thus precipitating the mixed hydroxides of columbium and tantalum. After being thoroughly washed by decantation, the hydroxides were dissolved in hydrofluoric acid, the solution filtered and treated with potassium fluoride, whereupon potassium tantalum fluoride precipitated out, while the more soluble potassium columbium oxy-fluoride remained in solution. The double fluorides were purified by recrystallization according to the method outlined by Balke (J. Am. Chem. Soc., 1905, 27, 1140-1157). Rubber and platinum dishes were used exclusively throughout this work. The tantalum double salt appeared as fine needles difficultly soluble in water. The columbium salt however was in the form of thin plates, very soluble in water. These salts were treated in large platinum dishes with sulphuric acid and evaporated until fumes of sulphuric anhydride disappeared. The resulting oxides after being thoroughly washed by decantation, were dried and used in the following experiments.

Methods of Analysis.

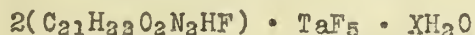
The tantalum or columbium in each case where an organic base was present, was determined as the oxide. The weighed sample was treated with a few drops of concentrated sulphuric acid and heated gently at first to expel the hydrofluoric acid and sulphur trioxide and finally heated strongly in the blast lamp to remove last traces of carbon.

The fluorine, in the case of the salts having weak organic bases, was determined by direct titration of the water solution with



standard sodium hydroxide solution using phenolphthalein as an indicator, but the remaining salts, having present in their molecules a strong base such as the tetra methyl ammonium salt, could not be titrated thus, since the strong base held back some of the fluorine. For the latter salts Opperman's method (Classen, Harriman, p. 152) was used. The weighed sample was placed in a flask containing silica and then treated with sulphuric acid at a temperature of 170° C - the silicon tetrafluoride being conducted into water and the hydrofluosilicic acid thus formed titrated with standard alkali.

Strychnine Tantalum Fluoride

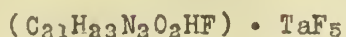


Thirteen grams strychnine were dissolved in the least possible amount of hydrofluoric acid and to the filtered solution there was added a solution of 5 grams of tantalum oxide in hydrofluoric acid. A voluminous white precipitate came down immediately. This was taken up with about 600 cc. of hot water and filtered, a large part of the precipitate remaining undissolved. The crystals from this filtrate gave the following analysis:

	Found
Ta ₂ O ₅	21.39
F	12.70

The crystals were needle like in structure and comparatively soluble in hot water.

Strychnine Tantalum Fluoride



This salt was obtained by recrystallizing the residue from the above salt. It was granular in structure and soluble with difficulty in hot water. The analysis gave:

	Calculated	Found
Ta ₂ O ₅	35.17	34.97
F	18.07	18.93

Benzylamine Tantalum Fluoride

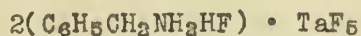


This salt was prepared by bringing together in solution the requisite amounts of benzylamine and the hydrofluoric acid solution of tantalum oxide. After recrystallizing several times from strong acid the salt was analyzed and gave the following results:

	Calculated	Found
Ta ₂ O ₅	54.95	54.54
F	28.22	28.19

This salt was in the form of long needles very soluble in water.

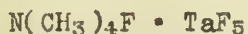
Benzylamine Tantalum Fluoride



This salt was prepared by recrystallizing the above salt from water free from acid, after adding an excess of benzylamine. The following is the analysis of the salt which was in the form of flat plates:

	Calculated	Found
Ta ₂ O ₅	41.81	41.01 42.51
F	25.05	24.41

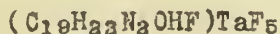
Tetramethylamine Tantalum Fluoride



Forty grams of a 10 per cent. solution of tetra methyl ammonium hydroxide were added to a solution of 5 grams of tantalum oxide in hydrofluoric acid. A fine white precipitate resulted. Upon recrystallization twice from water containing a very little acid, fine colorless granular crystals were obtained.

Analysis:	Calculated	Found
Ta ₂ O ₅	60.00	60.01
F	30.81	31.39

Chinconidine Tantalum Fluoride



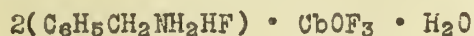
To 5.6 grams chinconidine in hydrofluoric acid solution were added a hydrofluoric acid solution of 5 grams tantalum oxide. The precipitate obtained was slightly yellow in appearance. After recrystallizing several times from a slightly acid solution, the salt gave the following analysis:

	Calculated	Found
Ta ₂ O ₅	35.63	35.13
F	22.32	22.85

The crystals were in the form of large needles slightly yellow in color, very soluble in hot water.

Columbium Salt

Benzylamine Columbium Fluoride



This salt was prepared by adding together in solution in hydrofluoric acid, the requisite amounts of benzylamine and columbium oxide. The salt came down after recrystallizing as beautiful symmetrical crystals. The analysis shows the presence of a molecule of water, which we would expect to find in such a salt.

Analysis:	Calculated	Found
Cb_2O_5	30.44	30.45
F	21.66	22.27





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